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ORIGINAL ARTICLE

# A convenient method for the oxidative aromatization of novel tetrahydrochromeno[4,3-b]quinolines with nitric acid

**Mohammad Reza Rezaei** [a,*], **Maryam Sarvaretaherabadi** [b]

[a] *Department of Chemistry, Faculty of Science, Payame Noor University, Sari, Iran*
[b] *Department of BioChemistry, Faculty of Medicine, Zahedan University of Medical Sciences, Zahedan, Iran*

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Aromatization;
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**Abstract** Nitric acid was used as a highly effective oxidizing agent for the very fast oxidative aromatization of novel tetrahydrochromeno[4,3-b]quinoline derivatives at ambient temperature with excellent yields.


## 1. Introduction

The hantzsch 1,4-dihydropyridine reaction between 4-aminocoumarin (Bossert et al., 1981; Nakayama and Kasoaka, 1996) and 2-benzylidene-cyclohexane-1,3-dione derivatives is a powerful synthetic tool for constructing N-containing six-membered heterocyclic compounds as well as in the synthesis of natural products including chromeno[4,3-b]quinoline derivatives (Cravotto et al., 2001; Simon et al., 2003; Shipman, 1994; Makioka et al., 1995; Yamanaka et al., 2000).

Chromeno[4,3-b]quinoline derivatives are found to exhibit a wide range of biological activities (Helmchen et al., 1986; Yamanaka et al., 2000), including psychotropic, anti-allergic, anti-inflammatory and estrogenic behavior (Munoz et al., 1982; Yamada et al., 1992; Lee et al., 2004). Among them, tetrahydrochromeno[4,3-b]quinolines are an important class of 1,4-dihydropyridines (DHPs) and NADH models (Fig. 1).

In the human body, 1,4-dihydropyridine compounds are oxidized to pyridine derivatives by the action of cytochrome P-450 in the liver (Guengerich et al., 1991). The oxidation of 1,4-DHPs to the corresponding pyridine derivatives constitutes the principal metabolic route in biological systems as well as a facile access to the corresponding pyridine derivatives (Stout and Meyers, 1982), which show anti-hypoxic and anti-ischemic activities from the easily available DHPs (Khadikar and Borkat, 1998; Sabitha et al., 2003). Therefore, oxidative aromatization of tetrahydrochromenoquinolines has attracted continuing interests of organic and medicinal chemists and a plethora of protocols has been developed.

## 2. Result and discussion

Initially a series of novel tetrahydrochromeno[4,3-b]quinolines were prepared via the condensation of 4-aminocoumarin and 2-Benzylidene-cyclohexane-1,3-dione derivatives under a solvent free condition at 200–220 °C according to our recently

* Corresponding author. Tel./fax: +98 9366799944.
E-mail address: shimi50@yahoo.com (M.R. Rezaei).
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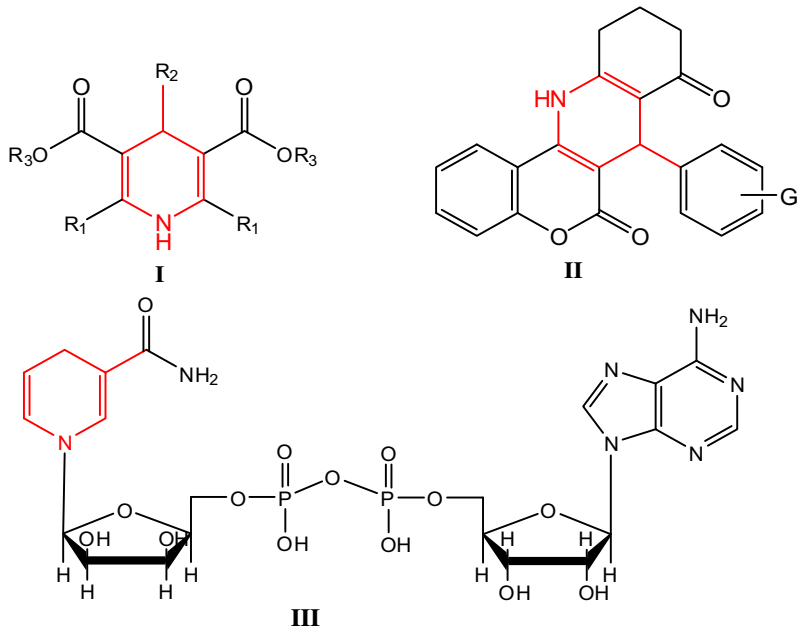
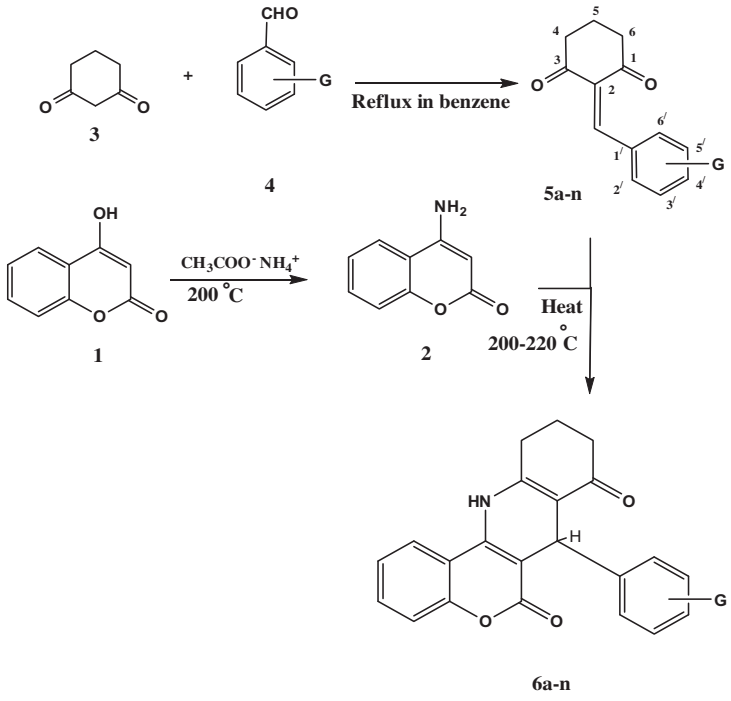



**Figure 1** Structure of Hantzsch 1,4-DHPs I, chromeno[4,3-b]quinolines II and NADH III.

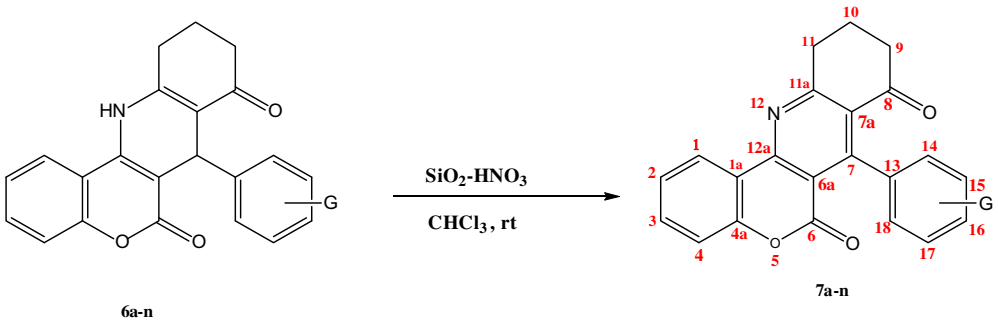



**Scheme 1**

reported work (Miri et al., 2011), and they were used to investigate their conversion into corresponding pyridines (Scheme 1).

Therefore a variety of 7-Aryl-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8-dione derivatives (**6a-n**) were subjected to aromatization via a combination of Supported nitric acid on silica gel in chloroform at room temperature with excellent yields (Scheme 2).

Also the above reaction was experienced using other catalysts such as $CrO_3$ (Grinsteins et al., 1967), $MnO_2$ (Vanden Eynde et al., 1995) ferric nitrate (Khadikar and Borkat, 1998; Sadeghi et al., 2001; Vanden Eynde and Mayence, 2003) nicotinium dichromate (Sadeghi et al., 2000) and Multi-wall carbon nanotubes modified with manganese complex (MWNTs) but the yields were unsatisfactory (Siswana et al., 2008). This reported oxidation procedure is very simple, efficient and heterogeneous for the oxidative aromatization of novel tetrahydrochromeno[4,3-b]quinoline derivatives using supported nitric acid on silica gel in a short reaction time at room temperature. The products are easily isolated from the




**Scheme 2**

**Table 1** Oxidative aromatization of novel tetrahydrochromeno[4,3-b]quinolines with $SiO_2$–$HNO_3$ in chloroform at room temperature.

| Grop G | Substrate | Product | Time (min) | MP (°C) | Yield (%)[a] |
|---|---|---|---|---|---|
| o-$CH_3$ | 6a | 7a | Immed | 210–212 | 94 |
| m-$CH_3$ | 6b | 7b | Immed | 172–174 | 95 |
| p-$CH_3$ | 6c | 7c | Immed | 241–243 | 98 |
| o-$OCH_3$ | 6d | 7d | Immed | 180–182 | 93 |
| m-$OCH_3$ | 6e | 7e | Immed | 155–157 | 94 |
| p-$OCH_3$ | 6f | 7f | Immed | 185–187 | 97 |
| o-Cl | 6g | 7g | Immed | 253–255 | 96 |
| m-Cl | 6h | 7h | Immed | 188–190 | 97 |
| p-Cl | 6i | 7i | Immed | 281–283 | 98 |
| m-$NO_2$ | 6j | 7j | Immed | 161–163 | 95 |
| p-$NO_2$ | 6k | 7k | Immed | 265–267 | 97 |
| m-Br | 6l | 7l | Immed | 184–186 | 96 |
| p-Br | 6m | 7m | Immed | 279–281 | 97 |
| H | 6n | 7n | Immed | 121–123 | 98 |

[a] Isolated yield.

reaction media by simple filtration and evaporation of $CHCl_3$. It is interesting to note that no side reaction such as nitration of tetrahydrochromenoquinolines including activation of an aromatic moiety was observed in this investigation (Table 1).

In summary in this paper we have introduced another ability of $SiO_2$–$HNO_3$ as an efficient oxidizing agent for the oxidation of tetrahydrochromeno[4,3-b]quinolines under mild and heterogeneous conditions. Also the cheapness and availability of the reagent, easy and clean work-up and excellent yields make this method attractive for chemists.

## 3. Experimental

### *3.1. Materials and apparatus*

Chemicals and all solvents used in this study were purchased from Merck AG and Aldrich Chemical. Melting points were determined on a Kofler hot stage apparatus and are uncorrected. The IR spectra were obtained on a Shimatdzu 470 spectrophotometer (potassium bromide disks).$^1$H NMR spectra were measured using a Bruker FT-500 spectrometer, and chemical shifts are expressed as $\delta$ (ppm) with tetramethylsilane as internal standard. The mass spectra were run on a Finnigan TSQ-70 spectrometer at 70 eV. Merck silica gel 60 F254 plates were used for analytical TLC; column chromatography was performed on Merck silica gel (70–230 mesh). Yields are purified products and were not optimized.

### *3.2. Typical procedure for the oxidative aromatization of 7-aryl-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8-dione derivatives*

To a solution of compound **6** (5.4 mmol) in $CHCl_3$ (5 mL), $SiO_2$–$HNO_3$ (0.6 g) was added. Reaction mixture was stirred at room temperature for 2 min (the reaction progress was monitored by TLC) and then filtered. Finally the filtrate was evaporated to dryness under reduced pressure, and the crude product was purified by short column chromatography and product **7** was obtained in excellent yield.

### *3.3. Characteristic data of new compounds*

#### *3.3.1. 7-(2-Methylphenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7a)*

Yield = 94%, Mp = 210–212 °C.

IR (KBr) $\nu$: 2922, 2848 (C–H aliphatic), 1754 (C=O ester), 1691 (C=O ketone), 757 (C–H oop) $cm^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz), $\delta$ (ppm): 2.02 (s, 3H, $CH_3$), 2.24 (m, 2H, $J$ = 6.6 Hz, $H_{10}$), 2.66 (t, 2H, $J$ = 6.6 Hz, $H_9$), 3.38 (t, 2H, $J$ = 6.6 Hz, $H_{11}$), 6.81 (d, 1H, $J$ = 7.0 Hz, $H_{15}$), 7.23 (t, 1H, $J$ = 7.0 Hz $H_{17}$), 7.28–7.35 (m, 3H, $H_{16}$, $H_{18}$, $H_4$), 7.40 (t, 1H, $J$ = 8.0 Hz, $H_2$), 7.61 (t, 1H, $J$ = 8.0 Hz, $H_3$), 8.68 (d, 1H, $J$ = 8.0 Hz, $H_1$).

$^{13}$C NMR ($CDCl_3$-d), $\delta$: 20.01, 20.98, 34.61, 40.13, 115.13, 116.90, 118.83, 124.61, 124.89, 125.58, 126.09, 127.44, 127.69,

129.26, 133.33, 134.24, 137.84, 153.43, 154.13, 156.39, 157.92, 169.58, 196.14.

MS: m/z (%), 355 ($M^+$, 44), 340 (44), 327 (37), 299 (100), 271 (37), 151 (50), 126 (50), 114 (63), 100 (44), 87 (25).

*3.3.2. 7-(3-Methylphenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7b)*

Yield = 95%, Mp = 172–174 °C.

IR (KBr) *v*: 2848 (C–H aliphatic), 1754 (C═O ester), 1691 (C═O ketone), 757 (C–H oop) $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz), $\delta$ (ppm): 2.24 (m, 2H, $J$ = 6.6 Hz, $H_{10}$), 2.39 (s, 3H, $CH_3$), 2.67 (t, 2H, $J$ = 6.5 Hz, $H_9$), 3.36 (t, 2H, $J$ = 6.5 Hz, $H_{11}$), 6.91 (m, 2H, H14, $H_{16}$), 7.24 (d, 1H, $J$ = 7.5 Hz, $H_{18}$), 7.30 (d, 1H, $J$ = 8.0 Hz, $H_4$), 7.33 (t, 1H, $J$ = 7.5 Hz, $H_{17}$), 7.39 (t, 1H, $J$ = 8.0 Hz, $H_2$), 7.60 (t, 1H, $J$ = 8.0 Hz, $H_3$), 8.67 (d, 1H, $J$ = 8.0 Hz, $H_1$).

$^{13}C$ NMR ($CDCl_3$-d), $\delta$: 20.93, 21.64, 34.56, 40.33, 115.08, 116.83, 118.80, 123.34, 124.56, 125.67, 126.11, 126.78, 127.74, 128.41, 133.25, 133.40, 137.35, 153.41, 153.86, 156.60, 158.13, 169.29, 196.39.

MS: m/z (%), 355 ($M^+$, 48), 340 (38), 265 (38), 149 (86), 121 (100), 105 (23), 92 (35), 71 (35), 57 (42), 43 (50).

*3.3.3. 7-(4-Methylphenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7c)*

Yield = 98%, Mp = 241–243 °C.

IR (KBr) *v*: 3033 (C–H aromatic), 2853 (C–H aliphatic), 1750(C═O ester), 1698 (C═O ketone), 759 (C–H oop) $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz), $\delta$ (ppm): 2.24 (m, 2H, $J$ = 6.6 Hz, $H_{10}$), 2.46 (s, 3H, $CH_3$), 2.68 (t, 2H, $J$ = 6.6 Hz, $H_9$), 3.37 (t, 2H, $J$ = 6.3 Hz, $H_{11}$), 7.02 (d, 2H, $J$ = 8.0 Hz, $H_{15}$, $H_{17}$), 7.27 (d, 1H, $J$ = 8.0 Hz, $H_{14}$, $H_{18}$), 7.32 (d, 1H, $J$ = 8.2 Hz, $H_4$), 7.41 (t, 1H, $J$ = 8.2 Hz, $H_2$), 7.61 (t, 1H, $J$ = 8.2 Hz, $H_3$), 8.68 (d, 1H, $J$ = 8.2 Hz, $H_1$).

$^{13}C$ NMR ($CDCl_3$-d), $\delta$: 20.94, 21.57, 34.54, 40.33, 115.19, 116.86, 118.84, 124.56, 126, 11, 126.15, 127.94, 128.75, 133.24, 134.93, 137.19, 153.42, 153.89, 156.67, 158.25, 169.27, 196.58.

MS: m/z (%), 355 ($M^+$, 100), 340 (31), 327 (25), 299 (19), 127 (13).

*3.3.4. 7-(2-Methoxyphenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione(7d)*

Yield = 93%, Mp = 180–182 °C.

IR (KBr) *v*: 3056(C–H aromatic), 2852(C–H aliphatic), 1749(C═O ester), 1693(C═O ketone), 753(C–H oop) $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz), $\delta$ (ppm): 2.25 (m, 2H, $J$ = 6.7 Hz, $H_{10}$), 2.69 (t, 2H, $J$ = 6.7 Hz, $H_9$), 3.38 (t, 2H, $J$ = 6.7 Hz, $H_{11}$), 3.74 (s, 3H, OMe), 6.90 (d, 1H, $J$ = 6.0 Hz, $H_{15}$), 6.89 (d, 1H, $J$ = 6.0 Hz, $H_{18}$), 7.00 (m, 1H, $J$ = 6.0 Hz, $H_{17}$), 7.31 (d, 1H, $J$ = 8.2 Hz, $H_4$), 7.41 (t, 1H, $J$ = 6.0 Hz, $H_{16}$), 7.43 (t, 1H, $J$ = 8.2 Hz, $H_2$), 7.61 (t, 1H, $J$ = 8.2 Hz, $H_3$), 8.68 (d, 1H, $J$ = 8.2 Hz, $H_1$).

$^{13}C$ NMR ($CDCl_3$-d), $\delta$: 20.97, 34.48, 40.06, 55.67, 110.39, 115.60, 116.82, 118.97, 120.73, 124.49, 126.04, 126.76, 127.40, 128.07, 129.21, 133.08, 153.32, 153.51, 153.87, 155.85, 158.13, 169.18, 196.28.

MS: m/z (%), 371 ($M^+$, 38), 340 (100), 120 (31), 91 (31), 75 (25).

*3.3.5. 7-(3-Methoxyphenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7e)*

Yield = 94%, Mp = 155–157 °C.

IR (KBr) *v*: 3060(C–H aromatic), 2835(C–H aliphatic), 1755(C═O ester), 1692(C═O ketone), 766(C–H oop) $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz), $\delta$ (ppm): 2.25 (m, 2H, $J$ = 6.5 Hz, $H_{10}$), 2.68 (t, 2H, $J$ = 6.5 Hz, $H_9$), 3.37 (t, 2H, $J$ = 6.5 Hz, $H_{11}$), 3.82 (s, 3H, OMe), 6.67 (s, 1H, $H_{14}$), 6.72 (d, 1H, $J$ = 7.5 Hz,$H_{18}$), 6.98 (d, 1H, $J$ = 7.5 Hz, $H^{16}$), 7.31 (d, 1H, $J$ = 8.0 Hz, $H_4$), 7.37–7.42(m, 2H, $H_{17}$,$H_2$), 7.61 (t, 1H, $J$ = 8.0 Hz, $H_3$), 8.68 (d, 1H, $J$ = 8.0 Hz, $H_1$).

$^{13}C$ NMR ($CDCl_3$-d), $\delta$: 20.91, 34.56, 40.29, 55.13, 112.49, 112.56, 115.02, 116.86, 118.76, 124.57, 126.11, 127.62, 128.97, 133.29, 133.89, 139.26, 153.41, 153.91, 155.96, 157.97, 159.33, 169.35, 196.17.

MS: m/z (%), 371 ($M^+$, 44), 340(37), 341 (50), 196 (63), 120 (38), 91 (100), 43 (50).

*3.3.6. 7-(4-Methoxyphenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione(7f)*

Yield = 97%, Mp = 185–187 °C.

IR (KBr) *v*: 2854 (C–H aliphatic), 1747 (C═O ester), 1688 (C═O ketone), 761 (C–H oop) $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz), $\delta$ (ppm): 2.24 (m, 2H, $J$ = 6.6 Hz $H_{10}$), 2.69 (t, 2H, $J$ = 6.5 Hz, $H_9$), 3.37 (t, 2H, $J$ = 6.4 Hz, $H_{11}$), 3.88 (s, 3H, OMe), 7.00 (d, 2H, $J$ = 8.7 Hz, $H_{15}$,$H_{17}$), 7.05 (d, 1H, $J$ = 8.7 Hz, $H_{14}$,$H_{18}$), 7.32 (d, 1H, $J$ = 8.2 Hz, $H_4$), 7.41(t, 1H, $J$ = 8.2 Hz, $H_2$), 7.62(t, 1H, $J$ = 8.2 Hz, $H_3$), 8.68 (d, 1H, $J$ = 8.2 Hz, $H_1$).

$^{13}C$ NMR ($CDCl_3$-d), $\delta$: 20.94, 34.54, 40.38, 55.11, 113.51, 115.29, 116.84, 118.85, 124.56, 126.12, 127.73, 128.11, 129.89, 130.03, 133.23, 153.40, 153.89, 156.37, 158.33, 169.25, 196.70.

MS: m/z (%), 371 ($M^+$, 11), 289 (18), 149 (29), 121 (32), 85 (63), 71 (88), 57 (100), 43 (95).

*3.3.7. 7-(2-Cholorophenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7g)*

Yield = 96%, Mp = 253–255 °C.

IR (KBr) *v*: 3068 (C–H aromatic), 2854 (C–H aliphatic), 1744 (C═O ester), 1690 (C═O ketone), 762 (C–H oop) $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz), $\delta$ (ppm): 2.27 (m, 2H, $J$ = 6.5 Hz, $H_{10}$), 2.69 (t, 2H, $J$ = 6.5 Hz, $H_9$), 3.41 (t, 2H, $J$ = 6.5 Hz, $H_{11}$), 7.03 (d, 1H, $J$ = 7.8 Hz, $H_{18}$), 7.27–7.43 (m, 4H, $H_2$, $H_4$, $H_{16}$, $H_{17}$), 7.50 (d, 1H, $J$ = 7.8 Hz, $H_{15}$), 7.62 (t, 1H, $J$ = 7.8 Hz, $H_3$), 8.70 (d, 1H, $J$ = 7.8 Hz, $H_1$).

$^{13}C$ NMR ($CDCl_3$-d), $\delta$: 20.88, 34.55, 39.89, 114.97, 116.94, 118.75, 124.68, 126.08, 126.68, 127.09, 127.18, 128.92, 130.77, 133.42, 133.90, 137.28, 152.92, 153.38, 154.26, 157.99, 169.69, 196.94.

MS: m/z (%), 377 ($M^+ + 2$, 33), 375 ($M^+$, 100), 340 (25), 187 (13), 127 (13), 113 (13), 100 (10), 87 (5).

*3.3.8. 7-(3-Cholorophenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7h)*

Yield = 97%, Mp = 188–190 °C.

IR (KBr) *v*: 3018 (C–H aromatic), 2853 (C–H aliphatic), 1744 (C═O ester), 1691 (C═O ketone), 757 (C–H oop bending) $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz), $\delta$ (ppm): 2.23–2.28 (m, 2H, $J$ = 6.5 Hz, $H_{10}$), 2.67–2.70 (t, 2H, $J$ = 6.5 Hz, $H_9$), 3.39–3.40 (t, 2H, $J$ = 6.5 Hz, $H_{11}$), 7.02 (d, 1H, $J$ = 7.0 Hz, $H_{16}$), 7.10 (s, 1H, $H_{14}$), 7.30 (d, 1H, $J$ = 8.0 Hz, $H_4$), 7.37–7.42 (m, 3H, $H_2$, $H_{17}$, $H_{18}$), 7.62 (t, 1H, $J$ = 8.0 Hz, $H_3$), 8.68 (d, 1H, $J$ = 8.0 Hz, $H_1$).

$^{13}$C NMR ($CDCl_3$-d) δ: 20, 34.57, 40.24, 114.86, 116.88, 118.64, 124.59, 124.72, 126.15, 126.27, 127.26, 127.62, 129.16, 133.49, 133.90, 139.79, 153.38, 154.04, 154.48, 158.07, 169.64, 196.08.

MS: m/z (%), 377 ($M^+ + 2$, 10), 375 (M+, 30), 340 (30), 319 (27), 289 (14), 227 (44), 127 (44), 120 (100), 100 (64), 87 (32), 74 (36).

*3.3.9. 7-(4-Cholorophenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7i)*

Yield = 98%, Mp = 281–283 °C.

IR (KBr) *v*: 2851 (C–H aliphatic), 1745 (C═O ester), 1691 (C═O ketone), 753 (C–H oop) $cm^{-1}$.

$^1$H NMR (CDCl3, 500 MHz), δ (ppm): 2.25 (m, 2H, *J* = 6.6 Hz H10), 2.68 (t, 2H, *J* = 6.6 Hz, H9), 3.38 (t, 2H, *J* = 6.6 Hz, H11), 7.05 (d, 1H, *J* = 8.3 Hz, H14, H18), 7.33 (d, 1H, *J* = 8.2 Hz, H4), 7.41 (d, 1H, *J* = 8.2 Hz, H2), 7.43 (d, 1H, *J* = 8.3 Hz, H15, H17),7.62(t, 1H, *J* = 8.2 Hz, H3), 8.68 (d, 1H, *J* = 8.2 Hz, H1).

$^{13}$C NMR (CDCl3-d), δ: 20.87, 34.56, 40.28, 114.85, 116.90, 118.62, 124.70, 126.16, 126.25, 127.64, 128.29, 133.47, 133.88, 136.46, 153.39, 154.07, 155.15, 158.08, 169.55, 196.34.

MS: m/z (%), 377 ($M^+ + 2$, 10), 375 (M+, 29), 289 (100), 265 (58), 237 (64), 121 (100), 85 (44), 71 (59), 57 (80).

*3.3.10. 7-(3-Nitrophenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7j)*

Yield = 95%, Mp = 161–163 °C.

IR (KBr) *v*: 3086 (C–H aromatic), 2849 (C–H aliphatic), 1748 (C═O ester), 1693 (C═O ketone), 1543, 1343 (N═O nitro aryl), 765 (C–H oop) $cm^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz), δ (ppm): 2.28 (m, 2H, *J* = 6.6 Hz $H_{10}$), 2.68 (t, 2H, *J* = 6.6 Hz, $H_9$), 3.39 (t, 2H, *J* = 6.6 Hz, $H_{11}$), 7.33 (d, 1H, *J* = 8.0 Hz, $H_4$), 7.42–7.48 (m, 2H, $H_2$, $H_{17}$), 7.61–7.66 (m, 2H, $H_3$, $H_{18}$), 7.98 (s, 1H, $H_{14}$), 8.31 (d, 1H, *J* = 7.75 Hz, $H_{16}$), 8.70 (d, 1H, *J* = 8.0 Hz, $H_1$).

$^{13}$C NMR ($CDCl_3$-d), δ: 20.78, 34.58, 40.16, 114.75, 116.94, 118.51, 123.21, 123.47, 124.94, 125.40, 126.25, 126.93, 128.82, 132.68, 133.77, 139.90, 148.09, 153.30, 154.34, 158.38, 170.06, 196.26.

MS: m/z (%), 386 ($M^+$, 30), 289 (37), 167 (62.5), 149 (51), 121 (29), 77 (98), 43 (100).

*3.3.11. 17-(4-Nitrophenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7k)*

Yield = 97%, Mp = 265–267 °C.

IR (KBr) *v*: 3072 (C–H aromatic), 2951, 2849(C–H aliphatic), 1741 (═O ester), 1689 (C═O ketone), 1547, 1346 (N═O nitro aryl), 765 (C–H oop) $cm^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz), δ (ppm): 2.25 (m, 2H, *J* = 6.4 Hz, $H_{10}$), 2.68 (t, 2H, *J* = 6.4 Hz, $H_9$), 3.39 (t, 2H, *J* = 6.4 Hz, $H_{11}$), 7.30 (d, 1H, *J* = 8.6 Hz, $H_{14}$, $H_{18}$), 7.33 (d, 1H, *J* = 8.2 Hz, $H_4$), 7.43 (t, 1H, *J* = 8.0 Hz, $H_2$), 7.64 (t, 1H, *J* = 8.0 Hz, $H_3$), 8.31 (d, 1H, *J* = 8.6 Hz, $H_{15}$, $H_{17}$), 8.70 (d, 1H, *J* = 8.0 Hz, $H_1$).

$^{13}$C NMR (CDCl3-d), δ: 20.79, 34.58, 40.12, 114.54, 116.98, 118.49, 123.44, 124.96, 126.26, 126.66, 127.15, 133.82, 145.80, 147.17, 153.35, 153.83, 154.35, 158.30, 170.04, 196.15.

MS: m/z (%), 386 ($M^+$, 12.5), 289 (34), 265 (18), 121 (80), 84 (100), 57 (75).

*3.3.12. 7-(3-Bromophenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7l)*

Yield = 96%, Mp = 184–186 °C.

IR (KBr) *v*: 3070(C–H aromatic), 2954 (C–H aliphatic), 1748 (C═O ester), 1693 (C═O ketone), 768 (C–H oop) $cm^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz), δ (ppm): 2.25 (m, 2H, *J* = 6.5 Hz, $H_{10}$), 2.69 (t, 2H, *J* = 6.5 Hz, $H_9$), 3.39 (t, 2H, *J* = 6.5 Hz, $H_{11}$), 7.08 (d, 1H, *J* = 7.6 Hz, $H_{16}$), 7.24 (s, 2H, $H_{14}$), 7.32, 7.35 (m, 2H, $H_4$, $H_{17}$), 7.41 (t, 1H, *J* = 8.0 Hz, $H_2$), 7.58 (d, 1H, *J* = 7.6 Hz, $H_{18}$), 7.64 (t, 1H, *J* = 8.0 Hz, $H_3$), 8.68 (d, 1H, *J* = 8.0 Hz, $H_1$).

$^{13}$C NMR ($CDCl_3$-d), δ: 20.85, 34.58, 40.24, 114.88, 116.91, 118.64, 122.04, 124.71, 125.03, 126.16, 127.22, 128.96, 129.38, 130.52, 133.50, 140.01, 153.40, 154.08, 154.40, 158.08, 169.61, 196.06.

MS: m/z (%), 421 ($M^+ + 2$, 98), 419 (100), 340 (33), 312 (68), 169 (80), 155 (38), 127 (67), 113 (70), 100 (60), 87 (47).

*3.3.13. 7-(4-Bromophenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7m)*

Yield = 97%, Mp = 279–281 °C.

IR (KBr) *v*: 3042 (C–H aromatic), 2922 (C–H aliphatic), 1745 (C═O ester), 1693 (C═O ketone), 771(C–H oop) $cm^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz), δ (ppm): 2.24 (m, 2H, *J* = 6.5 Hz, $H_{10}$), 2.67 (t, 2H, *J* = 6.5 Hz, $H_9$), 3.38 (t, 2H, *J* = 6.4 Hz, $H_{11}$), 6.98 (d, 1H, *J* = 8.3 Hz, $H_{14}$, $H_{18}$), 7.32 (d, 1H, *J* = 7.0 Hz, $H_4$), 7.40 (t, 1H, *J* = 7.0 Hz, $H_2$), 7.58 (d, 1H, *J* = 8.3 Hz, H15, $H_{17}$), 7.62 (t, 1H, *J* = 70 Hz, $H_3$), 8.67 (d, 1H, *J* = 7.0 Hz, $H_1$).

$^{13}$C NMR ($CDCl_3$-d), δ: 20.87, 34.56, 40.28, 114.92, 116.91, 118.68, 124.71, 126.16, 126.26, 127.40, 127.91, 131.19, 133.48, 136.99, 153.39, 154.08, 155.10, 158.23, 169.57, 196.34.

MS: m/z (%), 421 ($M^+ + 2$, 11), 419 ($M^+$, 11), 330 (13), 289 (100), 216 (22), 149 (20), 83 (31), 57 (76).

*3.3.14. 7-(Phenyl)-10,11-dihydro-6H-chromeno[4,3-b]quinoline-6,8-dione (7n)*

Yield = 98%, Mp = 121–123 °C.

IR (KBr) *v*: 3056 (C–H aromatic), 2949 (C–H aliphatic), 1744 (C═O ester), 1693 (C═O ketone), 776 (C–H oop) $cm^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz), δ (ppm): 2.25 (m, 2H, *J* = 6.6 Hz, $H_{10}$), 2.68 (t, 2H, *J* = 6.6 Hz, $H_9$), 3.38 (t, 2H, *J* = 6.6 Hz, $H_{11}$), 7.13 (m, 2H, $H_{14}$, $H_{18}$), 7.32 (d, 1H, *J* = 8.0 Hz, $H_4$), 7.42 (t, 1H, *J* = 8.0 Hz, $H_2$), 7.46 (m, 3H, H15, $H_{16}$, $H_{17}$), 7.61 (t, 1H, *J* = 8.0 Hz, $H_3$), 8.68 (d, 1H, *J* = 8.0 Hz, $H_1$).

$^{13}$C NMR ($CDCl_3$-d), δ: 20.91, 34.57, 40.30, 115.06, 116.87, 118.80, 124.59, 124.75, 126.13, 126.16, 127.56, 127.92, 133.30, 138, 153.43, 153.95, 156.38, 158.19, 169.38, 196.36.

MS: m/z (%), 341 ($M^+$, 81), 313 (69), 289 (38), 196 (44), 120 (75), 90 (100), 76 (44).

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